

Oxidation Kinetics of D-Ribose by μ - Peroxo Complex in Aqueous Medium

S. Ignatius Arockiam¹, A. Peter Pascal Regis²

^{1,2}Department of Chemistry, St. Joseph's College, Tiruchirappalli, India

ABSTRACT: A solution route method was carried out for the synthesis of μ -peroxo-bis [aminebis (ethylenediamine) cobalt(III)]perchlorate dihydrate. FT-IR and Electronic spectroscopic methods were used to characterize the synthesized complex. Biomimic oxidation of D-ribose by μ -peroxo complex has been studied kinetically in aqueous medium. Pseudo first order conditions has been followed to determine the rate of the reaction. The Oxidation reaction shows first order kinetics with respect to peroxo complex concentration and hydrogen ion concentration. The reaction rate points to negligible effect on increasing ionic strength. Potentiometric method was used to carry out the biomimic oxidation of the complex μ -peroxo complex. Thermodynamic and Arrhenius parameters were calculated and a plausible mechanism has been proposed.

KEYWORDS: Kinetics, Oxidation, peroxo complex, D-ribose, Activation parameters

I. INTRODUCTION

Living Systems are shaped by an enormous variety of biochemical reactions, nearly all of which are mediated by a series of remarkable biological catalyst known as enzymes [1]. The active catalyst contains the metal in its higher oxidation state so the transition metal ion with polydentate ligands as used as a model systems [2-3]. The oxidation of carbohydrates was widely studied by many researchers with different oxidants [4-9]. The peroxo complexes of cobalt (III) with different polyamines have been studied for effective model system. The present investigation on the oxidation of D-ribose with μ -peroxo complex has been studied extensively.

II. EXPERIMENTAL METHODS

The reagents employed were D-ribose (Loba AR), H_2SO_4 and Na_2SO_4 etc were of AR grade. All solutions were prepared in doubly distilled water. The $[(en)_2(NH_3)CoO_2Co(NH_3)(en)_2](ClO_4)_4 \cdot 2H_2O$ was prepared by bubbling oxygen through a solution containing cobaltous nitrate, sodium perchlorate and the appropriate ligand mixture. The complex was characterized by FT-IR and electronic spectroscopic studies. Typical kinetic runs were carried out under pseudo first order conditions $[D\text{-ribose}] \gg [\mu\text{-peroxo complex}]$. Appropriate amount of sulphuric acids, sodium sulphate, D-ribose and water was pipetted out in a double walled beaker provided with an inlet and outlet for water circulation from the thermostat set at desired temperature.

Requisite amount of μ -peroxo complex solutions was thermostated for half an hour and the kinetic reaction was started. The total volume of the reaction was 40 ml for the entire experiments. The cell [SCE/substrate-complex/pt] was used for the kinetics reaction with the reaction mixture and inserting the platinum and reference electrodes. The reaction mixture was stirred continuously using a magnetic stirrer throughout the experiment the emf of the cell was measured periodically using Equip-tronics potentiometer.

In order to study the effect of atmospheric oxygen, some experiments were carried out in an inert atmosphere by bubbling in nitrogen gas in the reaction mixture and it was ascertained that the velocity constants were reproducible within +2%. The

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

rate of the reaction was not much variation between air and inert atmosphere; hence the entire experiment was done in air atmosphere. Sodium sulphate was used to keep the ionic strength constant in the reaction mixture.

III. RESULTS AND DISCUSSIONS

Electronic spectrum

The single bridged μ -peroxo-bis[aminebis(ethylenediamine)cobalt(III)]perchlorate dihydrate shows an absorption band at 305 nm. The electronic spectrum shows that there is no characteristics transition in visible region, but the spectrum shows an intense charge transfer band near 205 nm. This band is due to the transfer of electron from the peroxide to metal. This band clearly prove that the presence of a single bridge peroxo ligand in the μ -peroxo complex.

FT-IR spectrum

The Perkin Elmer RSI spectrometer was used for the FT-IR characterization of the μ -peroxo complex using KBr pellet in the wave length region $400-4000\text{ cm}^{-1}$. The peaks at 3446, 3208, 2987 and 2385 cm^{-1} shows the presence of N-H stretching in the μ -peroxo complex. The nitrogen coordination present in the complex was affirmed by the peak at 2385 cm^{-1} . The presence of NH_3 , C- H and O-H bending vibrations were confirmed by the peaks obtained at 1508 cm^{-1} and 1381 cm^{-1} . The peaks at 1079 cm^{-1} gave evidence for the presence of C-N stretching and ClO_4 stretching vibrations in the μ -peroxo complex [10-12].

Table-1 FT-IR data for μ -peroxo complex

Wavelength(Cm^{-1})	Assignments
3446,3208,2987	$\nu(\text{NH}_2)_s$
2395	$\delta(\text{N-H})$
1588	$\rho(\text{NH}_2)$
1381	$\nu(\text{NH}_2)_s, \nu(\text{C-H})_b, \nu(\text{O-H})_b$
1079	$\nu(\text{C-N})$

S-Stretching, b-Bending, δ -Deformation, ν - bond stretching, ρ – rocking

All the kinetic runs were conceded out with [D-ribose] always ten times in excess of μ -peroxo complex. The oxidation of D-ribose was carried out with different initial concentration of μ -peroxo complex. The rate constants were increased by increasing the initial concentration of the complex. The reaction is first order with respect to complex.

Table-2 Effect of μ -peroxoComplex

[D-ribose] = $2.0 \times 10^{-2}\text{ mol dm}^{-3}$
[Na_2SO_4] = $2.5 \times 10^{-2}\text{ mol dm}^{-3}$

[H^+] = $2.0 \times 10^{-2}\text{ mol dm}^{-3}$

[peroxo complex] mol dm^{-3}	$10^4 k_{\text{obs}}\text{ S}^{-1}$
2.0	2.0
2.5	2.7
3.0	3.5
3.5	4.2

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

In order to study the effect of [D-ribose], the oxidation of the substrate was carried out with different initial concentration of the substrate. The reaction is zero order with respect to substrate.

Table-3 Effect of D-ribose

[complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$

10 ² [D-ribose] mol dm ⁻³	10 ⁴ k _{obs} S ⁻¹
2.0	2.0
2.5	2.1
3.0	2.2
3.5	2.1

The effect variation of added mineral acid concentration on the rate oxidation was studied by changing the concentration of added Sulphuric acid. The constant were found to be increased by increasing the hydrogen ion concentration. Hence the order with respect to hydrogen ion concentration was found to be one.

Table-4 Effect of Sulphuric acid

[D-ribose] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$

10 ² [H ₂ SO ₄] moldm ⁻³	10 ⁴ k _{obs} S ⁻¹
2.0	2.0
2.5	2.4
3.0	4.0
3.5	4.6

The effect of disparity of added salt on the rate of oxidation of D-ribose was studied by varying the concentration of added sodium sulphate. The rate of the reaction was virtually constant with increasing the initial concentration of added salt of the medium. This shows that the ionic strength is negligible on the reaction rate.

Table- 5 Effect of added Salt

[D-ribose] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$
 $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$

10 ² [Na ₂ SO ₄] moldm ⁻³	10 ⁴ k _{obs} S ⁻¹
2.5	2.0
3.0	2.0
3.5	1.8
4.0	2.0

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

The oxidation of D-ribose was carried out with different temperature. The rate constants were increased by increasing the temperature.

Table -6 Effect of Temperature

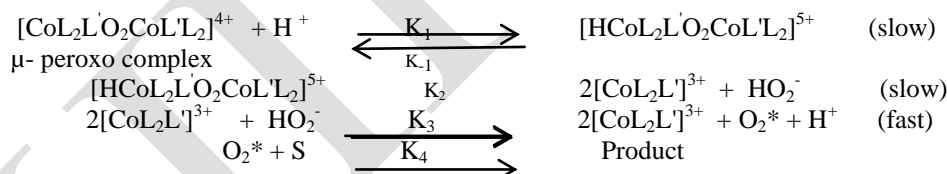
[D-ribose] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$
 [H⁺] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$

Temperature in K	$10^4 k_{\text{obs}} \text{ S}^{-1}$
313	2.0
318	3.0
323	4.1
328	4.8

The Arrhenius plot of $\log K_{\text{obs}}$ versus $1/T$ and the plot of $\log (K/T)$ vs $1/T$ gave a straight line with a very fine correlation. The energy of activation, enthalpy of activation, free energy of activation, entropy of activation and A were found to be 49.41 KJmol^{-1} , 46.81 KJmol^{-1} , 79.11 KJmol^{-1} , $-103.17 \text{ KJmol}^{-1}$ and 2.038 at 313k respectively. The positive value of free energy of activation ΔG^* and the enthalpy of activation designate that the transition state is extremely solvated while the negative entropy of activation ΔS^* suggests the formation of an activated complex with a reduction in the degree of freedom of molecules. It also suggests the compactness of the transition state as compared to the ground state and also in cyclic nature [13].

Mechanism and Rate law

In general, the mechanism of oxidation reactions [14] may be divided into three steps. Activation of molecular oxygen is the first step. The second step is the formation of reactive intermediate. The final step is the Transformation of intermediate into product is the final step. From the experimental results the most appropriate mechanism for the oxidation behavior of μ -peroxo complex is given as



At acidic condition the first step involves the formation of $[\text{CoL}_2\text{L}'\text{O}_2\text{CoL}'\text{L}_2]^{5+}$ complex ion from the peroxo complex and in this step there is equilibrium is obtained between the $[\text{CoL}_2\text{L}'\text{O}_2\text{CoL}'\text{L}_2]^{5+}$ and the peroxo complex. in the second step the $[\text{CoL}_2\text{L}'\text{O}_2\text{CoL}'\text{L}_2]^{5+}$ complex ion dissipate into Co(III) complex and HO_2^- ion. The products formed in the second step release activated oxygen with the concurrent reduction of mononuclear Co(III) complex to mononuclear Co(II) complex. This step supported by the mechanism which gives release of oxygen from a μ -peroxo complex Co(III) dimer[15]. The activated oxygen reacts with the substrate and gives the product in the final step. The above mechanism leads to the following rate law,

$$\text{Rate} = K_{\text{obs}} [\mu\text{-peroxo complex}] [\text{H}^+]$$

This rate law explains all the observed experimental facts.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

REFERENCES

- [1] Donald, J.Voet, "Principles of Bio-Chemistry", 3rd ed John Wileys sons, Newyork.
- [2] Goodwin, S., Witkop, B., "Quinol Intermediates in the Oxidation of Phenols and Their Rearrangements", J.Am.Chem.Sec., Vol.79, pp. 179-185, 1957.
- [3] LindBlad, B., LindStedt.G and Linstedt.S., "Mechanism of enzymic formation of homogentisate from p- hydroxyphenylpyruvate", J.Am.Chem.Soc., Vol.92, pp.7446-7449,1970.
- [4] Liang, Xi, Chang-jun, Liu and Pingyu, Kuai, "Selective oxidation of glucose to gluconic acid over argon plasma reduced Pd/Al₂O₃", Green Chem., Vol.10, pp.1318-1322,2008.
- [5] Srivastava.R.K.,Nath.N and M.P.Singh , " kinetics Studies of the Oxidation of Aldopentoses :L-Arabinose and D-Xylose Oxidized by Hexacyanoferrate(III) in an Alkaline Medium", Bull. Chem.Soc.Jpn, vol.39, spp.833- 837, 1966.
- [6] Azmat, R., and Nizami, S.S., "Reactivities of some aldoses towards iodine in alkaline", The Nucleus, Vol.42, No.(3-4), pp.177-184, 2005.
- [7] Odebunmi, E.O., Ogunlaja, A.S. and Owalude, S.O., "Kinetics of oxidation of D-arabinose and D-xylose by vanadium(V) in the presence of manganese II as homogeneous catalyst",Vol. 2, No.2, pp.127-139,2010.
- [8] Singh,A.K., Rahmani.A., Singh,V.K., Gupta,V., Kesarwani,D., Singh,B., "Iridium(III) catalysis of N- bromosuccinimide oxidation of reducing sugars in aqueous acid", Ind.J.Chem, Vol.40(A), 519, 2001.
- [9] Naz,R., Azmat,R., Khalil.A., Uddin,F., " Kinetics and mechanism of Oxidation of D-Galactose and D-Maltos with KMnO₄in Acidic medium by spectrophotometry", Asian J.chem., Vol.20, No.2, pp.829-837, 2008.
- [10] Casella, L. and Gullotti, M., "Synthesis, Stereochemistry, and Oxygenation of cobalt(II)- pyridoxal model complexes. A new family of chiral dioxygen carriers", Inorg.Chem.,Vol.25, No.9, pp.1293-1303,1986.
- [11] Silverstin., Bassler and Morill., "Spectroscopic identification of organic compounds", 4thed.,John Wiley & sons, Newyork.
- [12] Cotton,F.A., and Wilkinson,G., "Advanced inorganic chemistry", 5thed., John willey & sons,Newyork.
- [13] Weissberger,A., and Lewis,E.S., "Investigation of rates and mechanisms of reactions in techniques of chemistry", Newyork Willey,Vol.4, pp.421,1974.
- [14] Matsuura,T., "Bio-mimetic Oxygenation", Tetrahedron., Vol.33, No.22, pp.2869, 1977.
- [15] Ranganathan, C.K., Ramasami, T., and Santappa, M., " Acid decomposition reactions of diperoxo(amine)chromium(IV) complexes", Inorg.Chem., Vol.25, No.7, pp-915, 1986.